

Neutral dangling bonds may not be the dominant recombination centers for photoconductivity in hot-wire a-Si:H

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Abstract

We explored the properties of the recombination centers in a-Si:H films deposited by HW-CVD compared to that by PE-CVD. Thermally stimulated conductivity (TSC), electron spin resonance (ESR) and the constant photocurrent method (CPM) were measured before and after light soaking. We found that (a) the spectral lineshape of TSC and its light-induced changes show different features in HW- compared to those in PE-CVD films and (b) in the HW films the density of light-induced metastable defects, ΔN_d , from CPM is larger than the ΔD° from ESR; however, in the PECVD films ΔN_d is smaller than ΔD° . Some possible explanations are discussed.

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1. Introduction

A fundamental problem of a-Si:H is the light-induced metastable defect creation. The original Staebler–Wronski paper [1] describes that long exposure to light decreases both photoconductivity (PC) and dark conductivity (σ_d) in a-Si:H prepared by plasma-enhanced chemical vapor deposition (PE-CVD). The σ_d activation energy, E_a , increases due to metastable dangling bond (DB) creation near the middle of the gap [1]. Interestingly, the PC shows a relatively stable value and E_a decreases upon light soaking in a-Si:H films prepared by hot-wire (HW)-CVD [2]. In order to understand these anomalous photo-induced changes, we explored the properties of the recombination centers by measuring TSC, ESR and CPM. ESR measures the density of neutral dangling bonds D° and CPM takes into account all the electron transitions from gap states to the conduction band edge.

The TSC technique may not be as sensitive as deep-level transient spectroscopy (DLTS) to characterize the deep centers and may give misleading results. However,

based on the multiple-trapping model, Fritzsche and Ibaraki [3] developed the theory of TSC in amorphous semiconductors containing a continuous distribution of localized gap states. They found that neither the low- nor the high-temperature TSC peaks are caused by peaks in the energy dependence of the density of gap states. According to the model [3], in the initial period after the light is switched off, the thermal generation of carriers is balanced by recombination, and the form of the distribution function depends on the relative importance of either recombination or retrapping. Fig. 1a,b shows the distribution function. (a) For strong recombination, the recombination rate b_r is larger than the trapping rate, $b_r > b_t$. The quasi-Fermi level E_q is always below the demarcation energy E_d , and the carrier distribution function $f(E)$ has a sudden jump at E_d by the reduction of the mobile carrier density, n , due to strong recombination. (b) For weak recombination, $b_r < b_t$. At low temperatures E_q is above E_d and slowly moves down as the temperature increases, and finally reaches $E_q = E_d$. The carrier distribution function $f(E)$ has no sudden jump in the transition zone. In the case of strong recombination, the theory [3] predicts that there is a sudden rise near the transition from the initial rise to the steady-state regime. However, this case has never been observed in any a-Si:H-based films [3–5]. Hence,

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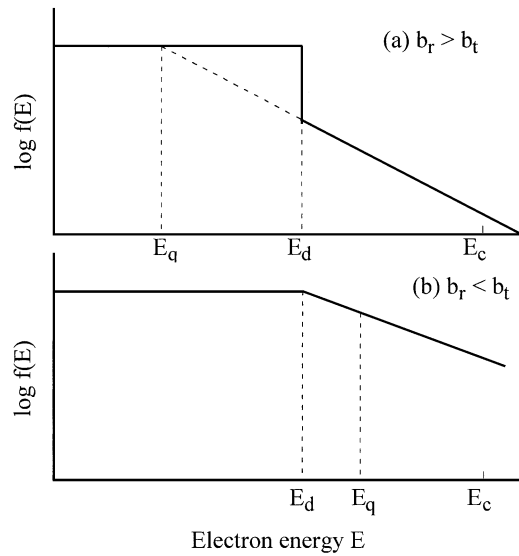


Fig. 1. Non-equilibrium carrier distribution function for (a) strong and (b) weak recombination relative to retrapping. E_d is the demarcation energy defined as $E_d = -kT \ln \nu_0 t$ that moves with time towards lower energy, E_q is the quasi-Fermi level and E_c is the electron mobility edge.

the commonly recognized recombination centers, D° , are sort of weak recombination centers with $b_r < b_t$. We do not analyze the whole TSC spectra here, but only pay attention to the transition zone from the initial rise to the steady-state regime.

2. Experimental

Device-quality intrinsic a-Si:H films were prepared by HW-CVD at the National Renewable Energy Laboratory (NREL) and by PE-CVD at BP-Solarex, United Solar Corp (USSC) and Kanazawa University. The film deposition conditions are listed in Table 1. The HW films H954 and H955 were deposited at a relatively low temperature using a separated deposition system. Their PC was not as stable as those deposited at high temperatures, but they still were more stable than PECVD

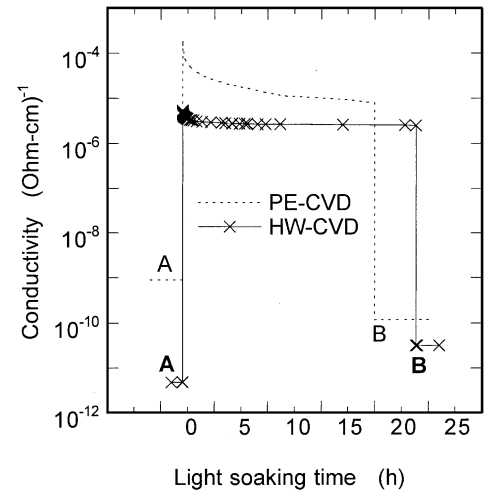


Fig. 2. The conductivity before, during and after light soaking for typical intrinsic a-Si:H films made by HW-CVD and PE-CVD. The solid line is for film T773, (T779 and T837 are similar) and the dotted line is for A7119 (PE#1 is similar).

films and their initial activation energy was larger than after being light-soaked.

In TSC studies, the MMR micro-probe system with vacuum of 10^{-4} Torr was used to mount the sample. The sample was first cooled down to 120 K and then exposed to the 632.8-nm laser light with an exposure time of $t_c = 60$ s. After a delay time, $t_o = 30$ min TSC was measured in a step-heating process with a constant heating rate of $\beta = 1.5$ K/min in the dark. Ohmic contact and a low field of 10^3 V/cm were used to avoid electrode effects. A Keithley 6512 programmable electrometer was used to record the current. The LABVIEW program was used for experimental control and data acquisition. Light soaking was performed in situ. The sample temperature was kept at 35 °C during light soaking. State A was reached after the sample was annealed in vacuum for 1 h at 160 °C; state B was reached by application of 200-mW/cm² white light through a water filter for 4 h. The details of ESR/CPM measurements can be found elsewhere [6,7].

Table 1
Sample preparation conditions

Sample ID	Growth method	Substrate T_s (°C)	Substrate	Reaction gas	Thickness (μm)	Supplier
T773	HW	360	Corning glass	SiH_4	1.1	NREL
T779	HW	360	Corning glass	SiH_4	0.45	NREL
T837	HW	400	Corning glass	SiH_4	1.2	NREL
A7119	DC-PE	200	Corning glass	SiH_4	3.0	BP-SLX
11961	RF-PE	~200	Corning glass	$\text{Si}_2\text{H}_6/\text{H}_2$	0.5	USSC
H954	HW	150	Quartz	SiH_4	0.7	NREL
H955	HW	250	Quartz	SiH_4	0.8	NREL
PE#1	RF-PE	250–300	Quartz	SiH_4	0.8	Kanazawa University

Table 2

Conductivity activation energy for annealed and light-soaked states

Sample ID	11961	A7119	H954	H955	T773	T779	T837
E_a (A) (eV)	0.92	0.73	0.86	0.95	0.98	1.05	0.96
E_a (B) (eV)	0.85	0.77	0.81	0.85	0.84	0.86	0.82

3. Results

Fig. 2 shows the typical photodegradation of PC and σ_d for device-quality intrinsic PE-CVD a-Si:H film deposited at 200 °C and HW-CVD film deposited at 320 < T_s < 440 °C. The dotted line represents the light-soaking effect for PE-CVD film, which shows a decrease in both PC and σ_d . Compared to the PE-CVD film, there is better PC stability and an increase in σ_d upon light soaking for the HW film. For the films listed in Table 1, the Fermi-level position is deduced from the conductivity activation energy according to $\sigma_d = \sigma_o \exp(-E_a/kT)$. We took the conductivity data from a temperature cycle of 270–420 K to deduce the activation energy. The values of E_a (A) and E_a (B) are listed in Table 2. It is evident that E_a moves in the opposite direction upon light soaking for the HW and PE-CVD films. The high-H-diluted PE-CVD film 11961 is an exception, for which E_f moves up. Fig. 3a,b shows the TSC curves for samples T779 and A7119 in states A and B. The most interesting feature is that a sudden rise occurs in the TSC near 200 K in the HW film for both states A and B, as shown in Fig. 3a. According to Fritzsche's theory [3], this is evidence of strong recombination centers. It means that the recombination rate for electrons b_r is larger than the trapping rate: $b_r > b_t$. D^+ , which has a larger capture rate for electrons than D° , is the candidate for the strong electron recombination center. A sudden rise in the TSC near 200 K has also been observed in the other HW films, T837 and T773, whereas a smooth transition in the TSC, similar to that for A7119, was observed for PE-CVD film 11961. Hence, the sudden rise in TSC is characteristic for the HW-CVD a-Si:H deposited at high substrate temperatures.

Regardless of Fritzsche's model [3], the sudden peak followed by a dip in TSC spectrum can be explained by the fact that a trap is emptying. It is evident in Fig. 3a for the HW film that the energy position of the two traps moved upwards towards the conduction band edge after light soaking, and a third trap is emptying just below room temperature in state B. On the other hand, two traps moved downwards in the PE-CVD film. These explanations are consistent with the opposite-direction movement of the Fermi-level positions upon light soaking in HW and PE-CVD films.

We have measured the density of defect states by ESR and CPM on two HW-CVD films deposited at

substrate temperatures of 150 and 250 °C in comparison to the PE-CVD film. Fig. 4a,b shows the CPM and ESR results for states A and B. For the ESR data, only the bulk defect density was counted by assuming that the density of surface defects is the same for all the films, based on the previous experimental results [8,9]. The light soaking results in an increase in defect density from 3 to $9 \times 10^{16} \text{ cm}^{-3}$ for all the films. The CPM data show a parallel increase in N_d , but the ESR data show a much larger increase in D° for the PECVD film than for the HW films. We plotted the density of light-induced metastable defects, $\Delta N_d = N_d(B) - N_d(A)$ and $\Delta D^\circ = D^\circ(B) - D^\circ(A)$, in Fig. 4c. The interesting thing is that for HW films ΔN_d deduced from CPM is larger than ΔD° , but for the PE-CVD film ΔN_d is smaller than ΔD° . The latter effect is commonly observed in PE-CVD film [6,7]. Assuming that the inhomogeneous

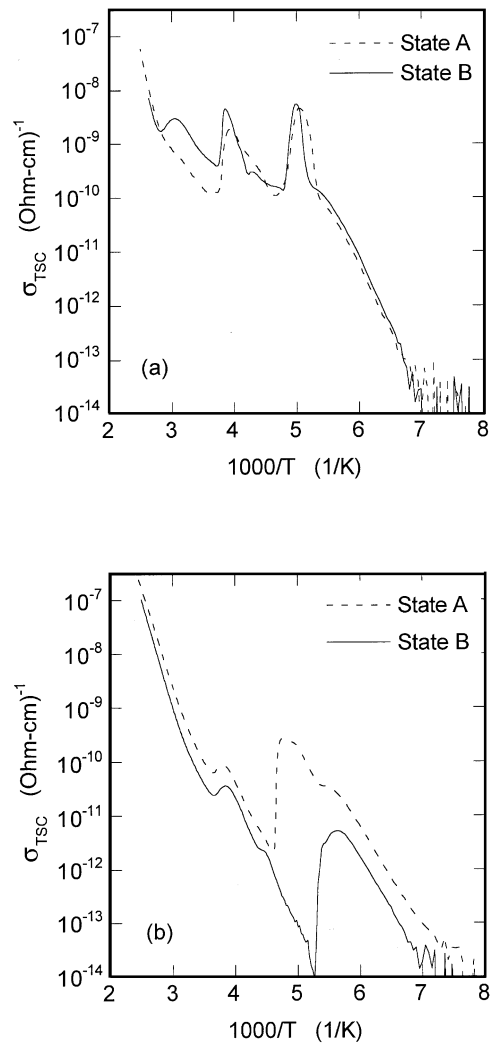


Fig. 3. Thermally stimulated conductivity in annealed state A and light-soaked state B: (a) for HW-CVD film T779 and (b) for PE-CVD film A7119.

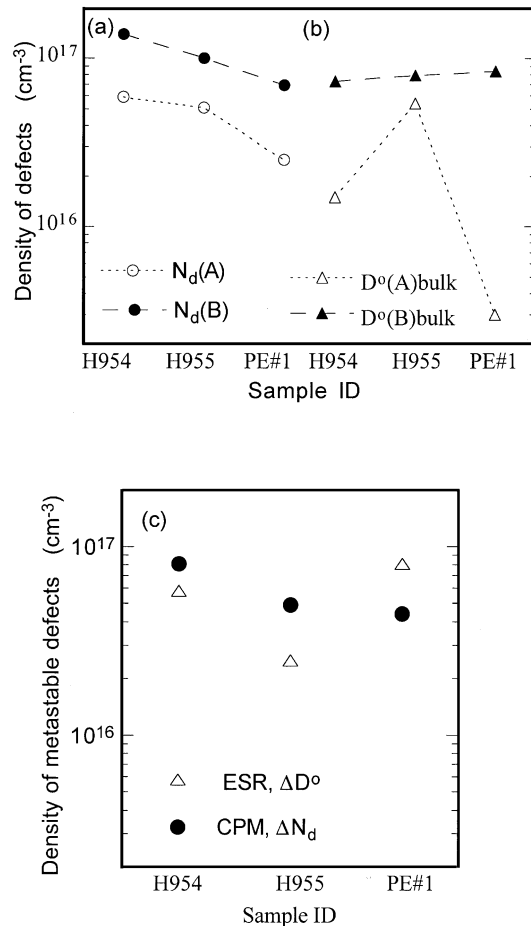


Fig. 4. The density of defects for HW- and PE-CVD films before and after 200-mW/cm² white light soaking for 30 h: (a) measured by CPM; (b) measured by ESR; and (c) light-induced metastable defects measured by CPM and ESR.

distribution of photocreated DBs is the same in all the films after the same light soaking processes, the different results between HW- and PE-CVD films can be explained by movement in the opposite direction of the Fermi level (E_f) upon light soaking, i.e. after light soaking, E_f moved upwards in the HW films, which left more negative charged defects, D^- , that are inactive to ESR. In the PECVD film after light soaking, E_f moved downwards, which resulted in more D^0 . This means fewer metastable electron recombination centers, D^0 , and hence less light-induced PC degradation in HW films compared to PE-CVD film. On the other hand, there are more metastable defects in a negative-charged state in HW films.

4. Discussion

The unusual photodegradation curve for HW-CVD films in Fig. 2 can be explained by one of two

mechanisms, as follows: (a) the upward movement of the Fermi-level, E_f , position: Assume that D^0 is the dominant recombination center and the electron lifetime is in inverse proportion to the density of D^0 . The creation of metastable DBs could be balanced by the upward movement of E_f , which results in filling of partial D^0 centers that are located below E_f . Therefore, the total number of D^0 , and thus the electron lifetime, could change much less than in the case of E_f moving downwards. The CPM/ESR results in Fig. 4 support these arguments. The alternative explanation of the TSC data in Fig. 3 also supports these arguments: (b) the existence of stronger electron recombination centers, such as positively charged defects, D^+ . We have shown evidence of strong recombination centers for electrons by thermostimulated current measurements. If D^+ rather than D^0 act as dominant recombination centers for both states A and B, the PC should be relatively stable upon light-induced D^0 creation. As is known, the capture rate of D^+ for electrons is much greater than that of D^0 . A density of 10¹⁵ cm⁻³ of D^+ among total defects of 10¹⁶ cm⁻³ would dominate the electron lifetime. Obviously, an increase in metastable D^0 of the order of 10¹⁶ cm⁻³ cannot change the electron lifetime much.

Alternatively, the TSC data point to the existence of a third trapping level that might be the shallow recombination center for HW-CVD films.

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References

- [1] D.L. Staebler, C.R. Wronski, Appl. Phys. Lett. 31 (1977) 292.
- [2] D. Han, G. Yue, H. Habuchi, E. Iwaniczko, Q. Wang, Thin Solid Films 395 (2001) 134.
- [3] H. Fritzsche, N. Ibaraki, Philos. Mag. B 52 (1985) 299.
- [4] N. Ibaraki, H. Fritzsche, J. Non-Cryst. Solids 66 (1984) 231.
- [5] M.F. Zhu, H. Fritzsche, Philos. Mag. B 53 (1986) 41.
- [6] T. Shimizu, M. Shimada, H. Sugiyama, M. Kumeda, Jpn. J. Appl. Phys. 40 (2001) 54.
- [7] T. Shimizu, M. Shimada, M. Kumeda, Jpn. J. Appl. Phys. 41 (2002) 2829.
- [8] T. Shimizu, H. Kidoh, A. Morimoto, M. Kumeda, Jpn. J. Appl. Phys. 28 (1989) 586.
- [9] T. Shimizu, H. Kidoh, M. Matsumoto, A. Morimoto, M. Kumeda, J. Non-Cryst. Solids 114 (1989) 630.